SYNTHESIS AND CHARACTERIZATION OF NOVEL MACROCYCLIC MOIETIES WITH N AND O-STUDY OF THEIR REACTIVITY TOWARDS METALLIC SUBSTRATES

DISSERTATION

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CHEMISTRY

BY

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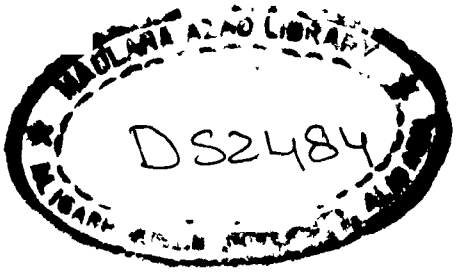

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CERTIFICATE

Certified that the work embodied in this dissertation entitled "*Synthesis and Characterization of Novel Macrocyclic Moieties with N and O - Study of their Reactivity towards Metallic Substrates*" is the result of original researches carried out under my supervision by Mr. Ajax.K.Mohamed and is suitable for the award of M.Phil degree (Chemistry) of Aligarh Muslim University, Aligarh.

(Dr. Mohammad Shakir)

Reader

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(AJAX K MOHAMED)

TO MY MOTHER

CONTENTS

INTRODUCTION

Macrocyclic ligands are multidentate cyclic molecules[1] consisting of an organic framework made up of heteroatoms which are capable of interacting with a variety of metal species. The three dimensional extention of macrocycles are the macropolycyclic ligands in which more than one macrocycle is incorporated in the same molecule. There is a wide range of interest in these molecules because of their unique and exciting chemistry. These can function as receptors for metal ions, molecular cations, neutral molecules or molecular ions of widely differing physical and chemical properties. These macrocyclic systems shows various interesting properties such as stable complex formation, transport capabilities and catalysis. Thus the association of two or more species with all the above features came to be known as supramolecular (macromolecular) chemistry.

The macrocyclic ligands containing multidentate centres have been the subject of considerable attention during recent years.[2] It is now well established that macrocyclic molecules containing the biting centers as $[N_4]$, $[N_2O_2]$, $[N_4O_2]$, $[N_4S_2]$ and $[N_2S_2]$ etc. display

unique and exciting chemistry in that they can stabilise unusual higher oxidation states of metal ions. They can function as receptors for substrates of widely differing physical and chemical properties and upon complexation can drastically alter these properties. Transport capabilities, stable complex formation, selective substrate recognition and catalysis are examples of wide ranging properties of these compounds.

The field macrocyclic chemistry have grown rapidly over the past 20 years that now an extensive series of macrocyclic ligands are available. Naturally occuring macrocyclic complexes of the porphyrin or corrin ring systems and the industrially important metal-phthalocyanine complexes have been studied for many years.[3] Synthetic ring complexes mimic some aspects of these naturally occuring complicated macrocyclic ring systems[4] and at present the study of such compounds are receiving much attention. A knowledge of the chemistry is being developed and the biochemical role of the metal ions in the natural systems is begining to be better understood eventhough the results obtained do not always closely parallel with those of the natural ones.

The chemistry of alkali and alkaline earth metal ions have witnessed a new dimension with the discovery of the binding properties of the cryptands[5] as well as natural macrocyclic antibiotics[6] and a few crown ethers[7]. The receptor capability is basically correlated with the design of the ligand. The size, nature and number of substrates to be complexed as well as the chemical reactivity of the resulting complexes are closely related with the ligand framework which in turn is determined by the number and nature of the binding sites and overall ligand geometry.

The macrocycles have been classified on the basis of donor atoms that is N,S,O,P,As and mixed donor systems and ofcourse topicity (mono-, di- or poly-topic). The cyclic polyethers of the "crown" type as shown in fig.1 have been investigated[7] and it has been found that these exibit an unusual behaviour towards a range of non-transition metal ions.[8]

A generalised synthetic route for macrocyclic crown ethers is well known and a few of this class could be obtained in fairly good yields through template methods.

However, majority of the polyethers exhibit low tendency to interact with transition metal ions.[9,10] Organometallic crown ethers are also reported and it has recently been shown[11] that a crown cation group can interact with appended transition metal acyl ligands. Complexes of this type have potential application in lewis acid accelerated alkyl migration to coordinated carbonyls.

Another category of macrocyclic ligands incorporates synthetic ring systems containing donor atoms other than oxygen. The majority of such ligands contain nitrogen donor atoms although ligands incorporating sulphur[12] as well as phosphorus[13] are also known. Thioethers analog of the crown have been known since long ago.[14] The sulphur macrocycles are found to show a preference to bind transition metal ions rather than alkali and alkaline earth ions.[15]

Macrocyclic ligands have been prepared by conventional organic synthesis as well as employing in-situ procedures involving cyclization in the presence of a metal ion. The crown polyethers are examples of

macrocycles which have been prepared mainly by direct synthesis.[8] Reactions shown by scheme (1) and (2) are examples of two synthetic routes for two such systems.

The tetraaza groups among the polyaza macrocycles have been the most extensively studied. Pentaaza and higher polyaza macrocycles have begun to appear more frequently, particularly in view of the potential of the larger macrocycles to bind more than one metal ion. This category includes ligands derived from schiff's base condensation of the appropriate moieties.[16] The polyaza analog of the crown ethers are also known and has been found to yield binuclear metal ion coordination.

Even though the synthetic methods used to prepare various macrocyclic ligands are easy, it is well known that there is a need in several areas for a rational approach towards ligand design for selective complexation of the metal ion in solution. Selection of donor atoms is based on ideas such as the hard and soft acid and base principle of Pearson or the A and B type acids of Schwarzenbach or Arhland et al. The idea of

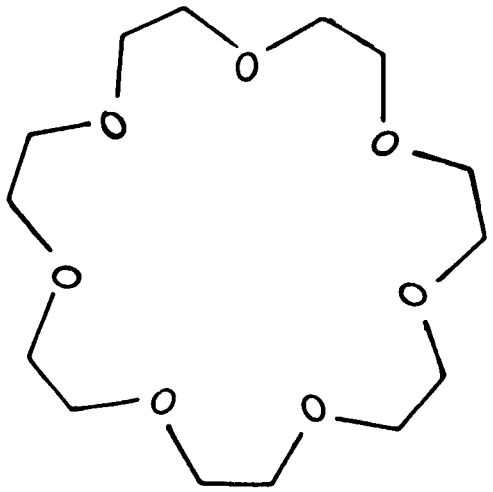
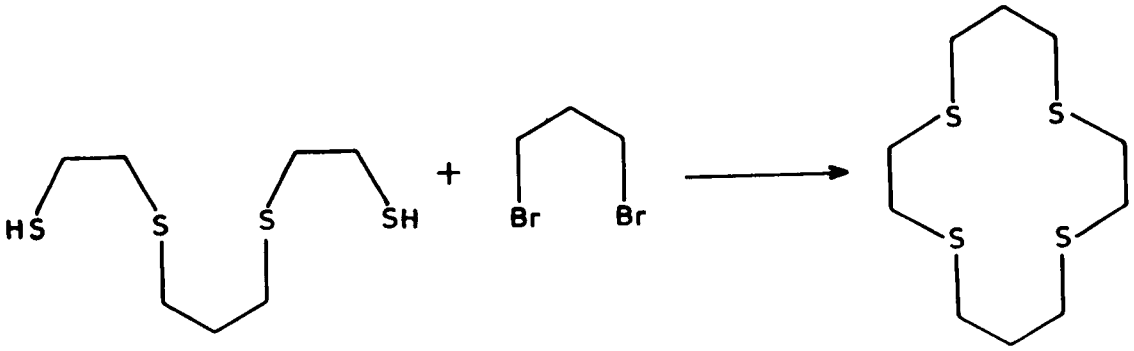
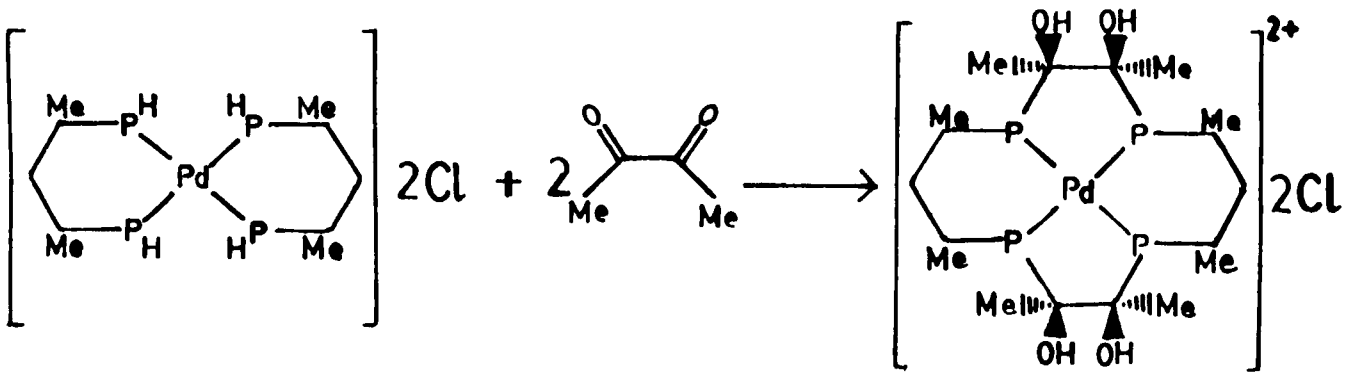


Fig-1



Scheme-1



Scheme-2

size match selectivity in macrocycles is less understood when we take the ligand design architecture. In this the metal ion will form its most stable complexes with the number of a series of macrocycles where the match in size between the metal ion and the cavity in the ligand is closest. Thus the size of the hole greatly influences[17] the properties of the complexes relative to those of open chain analogues. The cavity size can be related to ligand structure for both conjugated and non-conjugated ligands.[18] Thus the number of atoms in the ring is responsible for the 'hole size' for coordination.

The tetraphosphine macrocycle reported in 1975 is considered to be the first example of poly-phospha macrocycle.[19] Its template synthesis has also been reported.[20] The scarce reports on polyphospha macrocycle and their complexes is probably due to the fact that its synthesis involves lengthy procedure with poor yields.[21]

During recent years various physico-chemical methods specially electro-analytical techiques have been utilized to investigate the electropolymerization of the

ligand under suitable conditions. There are a few macrocyclic complexes which adopt a wide range of conformers of similar energies.[22] The conformation contain the best fit M-L length allowing strong binding to metal ions while lying coordinated out of the macrocyclic cavity. The N-donor and O-donor macrocycles show little diversity in the size selection towards metal ion compared to the corresponding open chain analogue. The macrocycles are rather too flexible to show geniue size match selectivity. Thus the chelate ring size and the size match selectivty of the donor atoms are controlled by the same factors that control the selectivity patterns of the open chain ligands.

Knowledge of substrate binding preferences and stereochemistry can be effectively utilized in the synthesis of novel receptor ligands by considering the geometry control into the receptor design. Interaction of the macrocyclic ligands and substrate can be fine tuned by appropriate selection of the binding sites, environment and overall ligand topology. The importance of both site and geometry can be considered by taking electronic effects as well as the structural effects.

It is well established that the chemical behaviour of the transition metal complexes, in general depends on their facile redox properties. This has been found more important for a large degree of natural and synthetic complexes involving macrocyclic ligands. These complexes undergo a diverse array of chemical reactions such as ligand oxidative dehydrogenation, metal alkylation, ligand substitution and hydrogenation. The success of some of these reactions has been closely linked to the ability of the higher and lower oxidation states of metal ions in these complexes to function as reactive intermediaties.

Olson and Vasilevskis[23] demonstrated the ability of macrocyclic ligands to stabilize a wide range of oxidation states of cordinated metal ion. Simultaneous and subsequent work conducted by D.H.Bush et al. and by Endicott and coworkers[24] has proven the generality of the above observations.

Macrocyclic complexes in general have the following characteristics.[25]

1. A marked kinetic inertness both to the formation of the complexes from the ligand and metal ion, and to the reverse, the extrusion of the metal ion from the ligand.
2. They can stabilize high oxidation states[26] - that are not normally readily attainable such as Cu(III) and Ni(III).
3. They have high thermodynamic stability - the formation constants for $[N_4]$ macrocycles may be orders of magnitude greater than the formation constants for non-macrocyclic $[N_4]$ ligands. Thus for Ni^{+2} the formation constant for the macrocyclic cyclam is about five orders of magnitude greater[27] than for the non-macrocyclic tetradentate ligand.

The additional enhancement in stability expected from gain in translational entropy cannot be attributed to the usual chelate effect that has been termed as the macrocyclic effect.[28] The differences in configurational entropy is because a greater loss in entropy would

be expected in the complexation of the open-chain ligand than in the macrocyclic ligand. The macrocyclic effect has both enthalpic and entropic components as compared to the chelate effect, which is largely entropic in origin. Thus for the macrocycle the donor atoms are constrained near the required coordination sites and so the ligand is prestrained to suggest additonal stability compared with the non-macrocycle. The macrocyclic effect is best understood by considering the thermodynamics[28,29] of the metal-complexation reactions. The configuration and solvation of the free macrocyclic ligand compared to the noncyclic ligand undoubtedly are very important contributors to this effect.

The synthesis of large fused-ring systems like the cryptates in which the entropy effects for ring closure are unfavourable, requires rather sophisticated methods.[30] For the synthesis of two nitrogen analogues of the polyether cryptates the above problem was overcome by doing the organic chemistry around a metal ion so that the large ring synthesis can be reduced to several small ring synthesis.[31] The possibility of encapsulation arose from the condensation reactions

between aldehydes and amines coordinated to Co(III). Endo and exo imine products[32] of the fig-2 and fig-3 were extraordinarily stable in acid solution and yet susceptiable to attack by nucleophiles at the imine-carbon atom. The reaction of the $[(en)_2CoC_2O_4]^+$ ion, for example, with formaldehyde in basic solution gave the dioxacyclam macrocyclic complex[33] in fig 2. This synthesis reavels that the carbinolamines and related imines which are formed, subsequently self-condense to give the cyclic ligand with out rupture of any metal-ligand bonds. These properties along with some ancient organic chemistry involving the self-condensation of NH_3 and CH_2O to yield "hexamine" indicates how a tris bidentate amine might be capped to yield a cage.

Some macrocyclic ligands render extraordinary stability to metal complexes against ligand substitution or dissociation by effectievly encapsulating the metal ions, as for examples the cryptates.[34,35] For the synthesis of macrocyclic ligands[36,37] condensation of amines with formaldehyde has been employed. The synthesis of Ni(II) complexes with different ligands

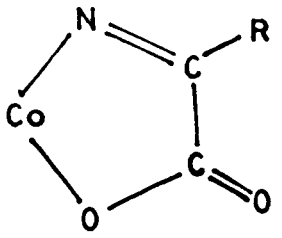


Fig-2

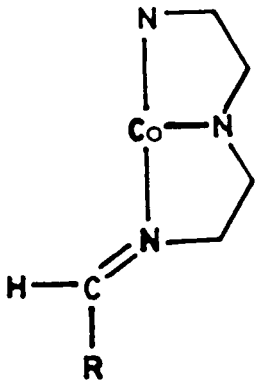


Fig-3

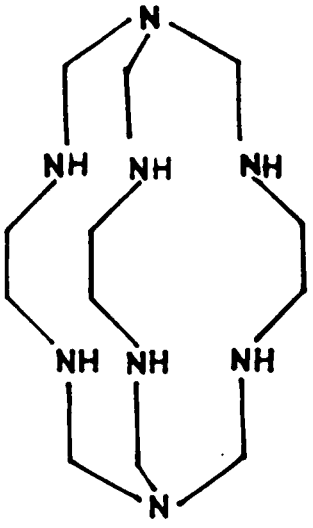


Fig-4

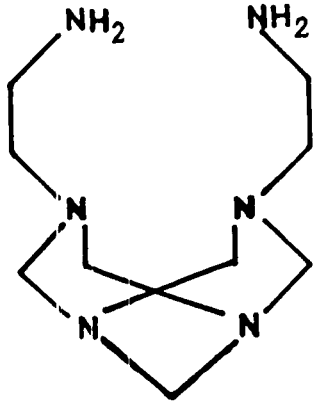


Fig-5

fig 4-6 by the template condensation of ethylenediamine, formaldehyde and ammonia was done by Suh et al.[36]

Large number of 14 membered macrocyclic ligands and their complexes have been synthesized and studied. With the same template condensation of amines and aldehydes in the presence of metal ions polydentate complex shown below by fig 7 and macrocyclic complex fig 8 and fig 9 have been synthesized.[37-39]

L.Fabbrizzi and coworkers[40] synthesized the metal complex of ligand L_a (fig-10) and studied the nature and role of the bridging tertiary amine group in macrocyclic complex. They prepared through the typical template procedure, the nickel(II) complex of the 14 membered pentaaza macrocycle ligand L_a which in addition to the four secondary amine nitrogen atoms of cyclam, contains just one methylamine bridging group. The X-ray investigation showed that in the $[Ni\ L_a]^{2+}$ cation only the four secondary amine nitrogen atoms were coordinated according to an almost regular stereochemistry. It also showed that the tertiary amine group of the azacyclam ring is not involved in direct coordination of the metal

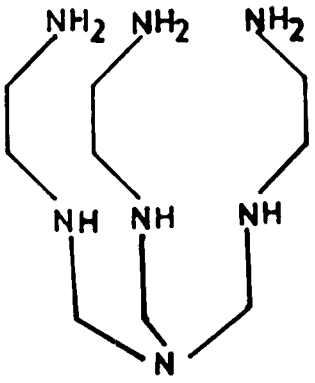


Fig-6

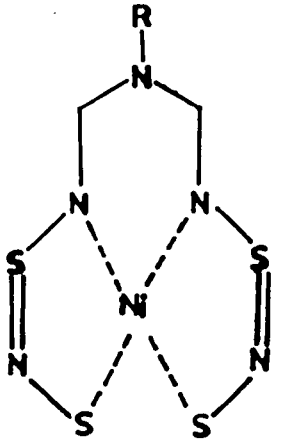


Fig-7

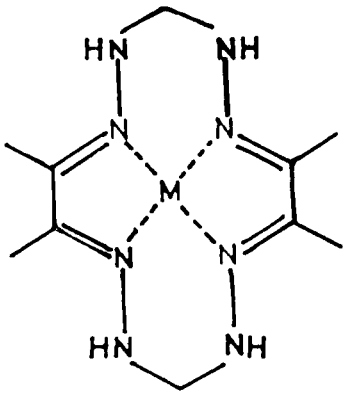


Fig-8

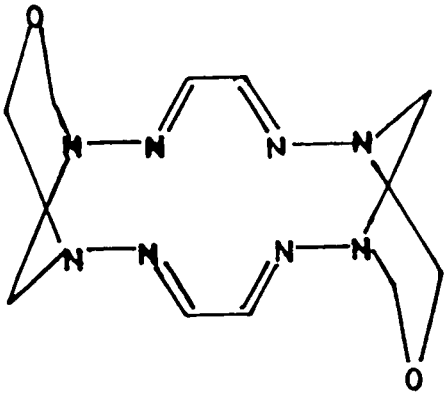


Fig-9

centre but its lone pair is exposed. Thus the tertiary nitrogen atom may behave as a rather strong base.

An attempt was made by Suh and Kang to synthesize 14-membered hexaaza macrocyclic ligand L_b (fig-11) by the condensation reaction of ethylenediamine, formaldehyde and ammonia in presence of Ni(II) ion instead they got fig 4, 5 and 6.[41,42]

Similarly it was reported that condensation of $[Co(en)_3]^{3+}$ with formaldehyde and ammonia produced the Co(III) complex of fig 11.[43] In these reactions, formaldehyde links two amine moieties, forming methylenediamine linkages ($N-CH_2-N$). The methylenediamine linkages are unstable when they contain primary and secondary amines and thus secondary nitrogens of ethylenediamines of the Ni(II) complexes of fig 4 and 5 are stabilized by the coordination of metal ion. The failure to synthesize the complex with ligand L_b (fig-11) was ascribed to the instability of methylenediamine linkages containing uncoordinated secondary nitrogens. Suh and Kang[44] successfully extended the systhesis of two dimensional systems i.e

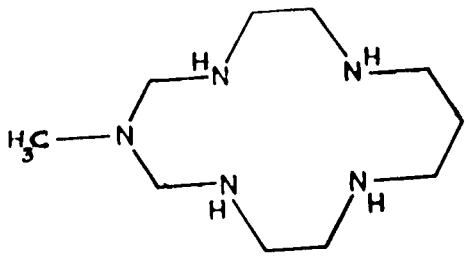


Fig-10

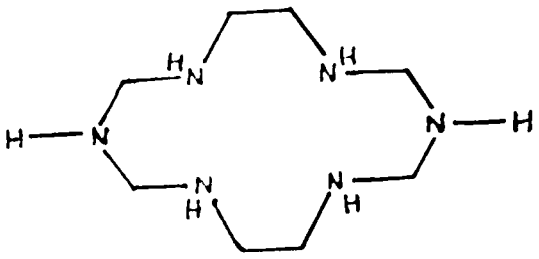


Fig-11

cyclam like macrocycles, by treating $[M^{II}(en)_2]^{2+}$, (M = Ni or Cu) with formaldehyde and a primary amine RNH_2 (R = CH_3 or C_2H_5).This condensation produced the 14-membered hexaaza macrocyclic ligand L_c (fig-12).

Studies in solution showed that $[Ni\ L_c]^{2+}$ exhibits properties very similar to $[Ni(cyclam)]^{2+}$ fig-13 sugesting that ligand L_c behaves as a quadridentate ligand: the two tertiary amine nitrogen atoms seem to play an architectural role and are not involved in the coordination.

The macrocyclic effect has been explained on the basis of equilibrium and calorimetry studies[45] carried out for $[Ni(cyclam)]^{2+}$ (fig-13) and $[Ni(2,3,2\text{-tet})]^{2+}$ (fig -14). Although it is quite reasonable to assign the macrocyclic effect to the entropy factor, the results of equilibrium and calorimetry studies suggest that the actual reason[46] for the greater stability of the macrocyclic complex is due to a more favourable change in entropy, H^o (a difference of -14 K cal/mol) which overcomes a less favourable change in entropy, S^o (a difference of -16 cal/C^o K mol) for the reaction. The

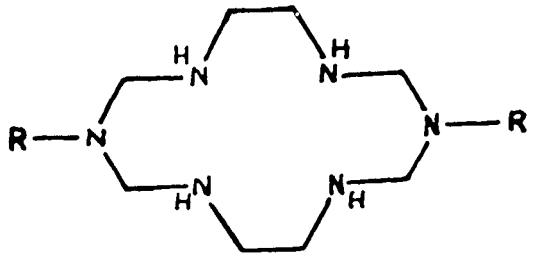


Fig -12

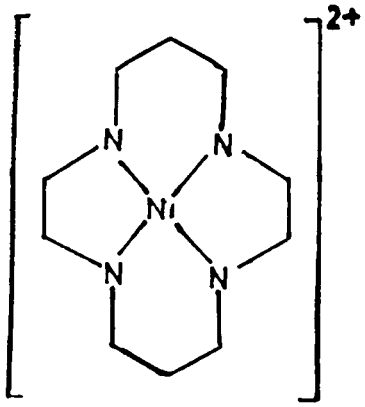


Fig-13

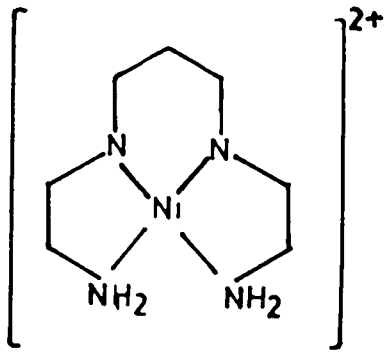


Fig-14

favourable change in enthalpy is well understood by considering the ligand solvation effect in the thermodynamics of the metal complexation reaction.

The effect of ligand solvation[47] permits several predictions. The macrocyclic effects should be independent of the metal as long as there is not an unfavourable geometry in the coordination of the metal ion with in the macrocycle. Similar enhancements of the stability constants are found for Cu^{2+} and Ni^{2+} with hexamethyl derivaties of cyclam. It is proposed that use of solvent with weaker primary solvation of the ligand will increase the relative contribution due to the configurational entropy, as the importance of solvation effect is diminished.

PRESENT WORK

The present work deals with the study of some novel macrocyclic ligands, their metal ion interaction and chemical behaviour upon complexation. An attempt for the synthesis of 14-membered hexaaza macrocyclic ligands by the condensation reaction of ethylenediamine, formaldehyde and benzidine was unsuccessful and the ligand could not be isloated. However a new polydentate ligand was synthesised and its reactivity towards a few metal ions was undertaken. New novel hexaaza macrocyclic complexes were also synthesized by the template condensation of ethylenediamine, formaldehyde and benzidine in the presence of the metal ions.

The newly synthesized compounds have been characterized using physico-chemical methods,viz, magnetic susceptibility measurements, IR, UV-visible spectroscopic studies. The work on template reactions and solution studies incorporating electro analytical technique could also be undertaken for a detailed insight in the chemistry of the newly synthesized macrocyclic ligands.

EXPERI MENTAL METHODS

It is well established that single X-ray crystallographic method is a worthwhile tool to get complete information regarding the molecular geometry of the compound indicating the exact disposition of the various atoms in the molecule, if a suitable crystal is grown. However, the complexes described in this work have been characterised by analytical methods, magnetic susceptibility and molar conductivity measurements, infrared and electronic spectral studies. Elemental analysis for carbon, hydrogen and nitrogen of the ligand and complexes were done at CDRI Lucknow and A.M.U Aligarh. The estimation of halogen was done gravimetrically[48] and the metals were estimated by titrating with standared E.D.T.A solution.[49] For the metal estimation, a known amount of the complex was decomposed with a mixture of nitric, perchloric and sulphuric acid and the halogen was estimated by fusing a known amount of the compound with fusion mixture (KNO_3 and K_2CO_3)

The infrared and far-infrared spectra were recorded as KBr-discs on IR 408 Shimadzu spectrophotometer. Reflectance spectra of the solid samples using MgO

dilutent and electronic spectra in DMSO were recorded on a Pye Unicam 8800 (philips,Holland) UV-Visible specrophotometer at room temperature. Results of the magnetic susceptibility measurements were obtained by using a Faraday balance at $30^{o}C$ caliberated with $Hg[Co(NCS)_4]$.

Though a detailed theory of the various techniques used for characterization of the compounds described in this book is available in text books, monographs or reviews, a brief description would not be inappropriate, as given in the following paragraphs.

I R SPECTROSCOPY

Infrared absorption spectra are commonly obtained by placing the sample in a beam of a double beam infrared spectrophotometer and measuring the relative intensity of transmitted light. When the infrared light of the same frequency is incident on the molecule the energy is absorbed and amplitude of that vibration is measured. When the molecule reverse from the excited state to the original ground state, the absorbed energy is released as heat. The occurence or non-occurence of

an infrared radiation is governed by the following selection rules.

1. In order for a molecule to absorb infrared radiation as vibrational excitation energy, there must be a change in the dipole movement of the molecule as it vibrates.
2. In absorption of the radiation, only transition for which change in the vibrational energy level is V=1 can occur, since most of the transition will occur from state V_0 to V_1 and the frequency corresponding to its energy is called the fundamental frequency.

The frequency of certain groups of atoms is called group frequency. These frequencies are characteristic of the group irrespective of the nature of the molecule in which these groups are attached. The absence of any band in the approximate region indicates the absence of that particular group in the molecule.

The infrared radiation is usually said to have wavelength lying between 0.8μ to 1000μ. The wave number i.e. the number of waves per centimeter is used to characterize the radiation.

Important Group Frequencies In The IR Spectra Of The Compounds Relavent For Characterization Of Compounds:-

1. ν(N-H) bands :-

Primary amines show a doublet for the (N-H) stretching band in the 3500-3200 cm^{-1} region while a single band is only observed for the secondary amine N-H bond in the 3350 cm^{-1} region. Primary amines shows N-H deformation frequencies in the region 1650-1590 cm^{-1} while secondary amines show N-H deformation frequencies in the region 1650-1550 cm^{-1}.

2. ν(C-N) and ν(C-H) bands:-

The (C-N) stretching vibrational band of secondary amines appear approximately in the 1350 cm^{-1} region. The C-H groups in the benzene ring shows vibrational bands at 3000 cm^{-1} and numerous bands in the 800-600 cm^{-1} regions which are assignable to (C-H) stretching and (C-H) deformation respectively.

3. ClO_4 stretching frequencies:-

The ClO_4 fundamental bands for the ionic complexes comes in the region 1050-1170 cm^{-1} and 930 cm^{-1}. For bidentate complexes the band comes in the region 1010-

1130 cm^{-1} and 910 cm^{-1}. Bidentate complexes shows band in the region 1270-1150 cm^{-1} and 1030 cm^{-1}.

4. M-N stretching vibrations:-

The M-N stretching frequency is of particular interest since it provides direct information about the coordinate bond. In complexes it generally appears in the region 420-350 cm^{-1}.

5. M-Cl stretching vibrations:-

The M-Cl stretching vibration generally appears in the region 300-260 cm^{-1}. The position and intensity varies for different metals.

UV-visible spectroscopy :-

Electronic spectra is a very powerful tool in coordination chemistry for the elucidation of structures of complexes. In transition metal complexes the electronic transition occur with in the various energy levels of a d orbital and therefore termed d-d transitions. For electronic transitions to occur by absorption of radiation several selection rules are set up. But these selection rules are relaxed in majority of

the complexes and if it were not for this reason the complexes would not absorb radiation and appear colourless. The energy of the absorbed light falls in the range of UV-visible radiations and therefore, also known as UV-visible spectra.

The spectra of transition metal complexes[50,51] generally shows at least two well defined absorption bands in the visibile region and a third band some times obscured by charge transfer bands in the high energy region. The spectra is interpreted with the aid of ligand field theory.

The ligand field splits the orbitals of the d level into various energy levels or states. Electronic transitions takes place between these energy levels or states giving rise to characteristic bands in the spectra. The extend of splitting is given as a function of Dq. The magnitude of Dq or ΔE varies with different ligands for different complexes. As Dq increases, ΔE, the energy of the transition increases. The value of ΔE(10 Dq or Δ) is obtained directly from the frequency of the absorption peak. The frequencies of each band

obtained from the electronic spectra is compared with the spectral data available for the expected geometry of the transition metal ion of interest. The frequencies associated with each band is then assigned to various energy levels or states between which the electronic transition occur. In order to represent the energy levels accurately Orgel and Tanabe-Sugano diagrams are made use off. The experimental energies obtained from the spectra are almost always lower than the values calculated. This deviation may be attributed to covalence (β) in the bonding which results in smaller values of β, the interelectronic repulsion parameter in complexes than that for the free ions.

Δ and β cannot be determined accurately. The interpretation of spectra becomes complicated. It is therefore necessary to consider the effect of factors like spin-orbit coupling and Jahn-Teller distortion on the energies of the levels. The effect of σ bonding and π bonding on the energy levels can be obtained by relating the energies of the observed d-d transitions to the energy levels associated with the complex. The number of bands, frequencies and molar absorptivity

should all be considered in interpreting the spectra. Molar absorptivity (ε) can be calculated by using Beer-Lambert's law relationship

$$A = \varepsilon bc \qquad \text{----------(3)}$$

where A is the absorbance, ε is the molar absorptivity or extinction coefficient, b is in the length of absorbing system and c is the concentration. Finally the spectra in solution should be checked against spectra of solids (refluctance or mulls) to be sure that drastic changes in structure do not occur in solution either through ligand displacement by solvent or through expansion of the coordination number by solvation.

Magnetic Susceptibility Measurements :-

Magnetic data when employed in conjunction with electronic spectra of transition metal complexes give important information regarding the structure and property of the complex.

Magnetic properties of substances arise from the magnetic moment resulting from motion of charged

electrons. But it is not possible to determine the magnetic moment directly. Instead the magnetic susceptibility is measured from which the moment is calculated. The volume susceptibility is defined by equation

$$\chi = I/H \qquad \text{----------(4)}$$

where I is the intensity of the magnetization induced by the field of strength, H, per unit volume of the substance. But often the susceptibility is defined as the weight susceptibility χ_g where

$$\chi_g = \chi \text{ /density} \qquad \text{----------(5)}$$

or it is defined as the molar susceptibility χ_m.

$$\chi_m = (M/d)\chi \qquad \text{----------(6)}$$

where m has the units cc mol^{-1}. For normal paramagnetic and dimagnetic substances, χ, χ_g and χ_m are constants independent of field strength. The susceptibility measured will have contribution from paramagnetic and dimagnetic susceptibilities, the former being much greater. The measured susceptibility should be corrected by subtracting the dimagnetic contribution. The magnetic moment is then calculated from the corrected susceptibility by equation (7)

$$\mu_{eff} = 2.84 \ (\chi'_A T)^{1/2} \qquad \text{---------(7)}$$

where T is the absolute temperature, χ'_A is the susceptibility of the constituent atoms corrected for diamagnetism using pascal's constants

χ'_A= measured susceptibility - diamagnetic susceptibility

-------(8)

and μ_{eff} is the magnetic moment of the compound in Bohr magnetons.

In principle, the method of measuring magnetic susceptibility [52] all depend up on the fact that when a material (dv,dm) is placed in an inhomogeneous magnetic field of value (H) it experiances a force (dF) along the field gradient (dH/dX) at the point dV. The force is given by equation 9

$$dF = H\chi \ dm \ \ dH/dX \qquad \text{----------(9)}$$

In practice there are two methods to measure this force :- the Faraday method which measures the force directly and the Gouy method which measures the force integrated over a large difference in field gradient. Gouy is most simple and reliable. Faraday method has the

advantage that only very small amount of specimen is required but the operation of the instrument is difficult.

Generally, one does not determine each of the constants in equation 9 but rather the apparatus calibrated with a standared substance, and below equation 10 is employed.

$$\chi_{unknown} = \frac{\Delta W_{unk}}{W_{unk}} \cdot \frac{W_{std}}{\Delta W_{std}} \cdot \chi_{std} \quad \text{----------(10)}$$

where χ is the gram susceptibility, W is the weight of the sample in field off condition and ΔW is the change in weight of sample in field on and field off condition.

The measured gram susceptibility is corrected for the dimagnetic effect and magnetic moment is calculated from equation 7. The experimentally determined magnetic moments of transition metal complexes do not agree very well with the calculated moments. The descrepency is accounted by considering factors like quenching of orbital angular momentum by ligand-fields, spin orbit coupling, TIP and other properties like ferromagnetism and antiferromagnetism. The magnetic moment deduced by

considering the above factors help in assertaining the number of unpaired electrons and distinguish spin paired from spin free complexes. It also gives informabtion regarding the oxidation state of the metal ion in a complex. The best application seems to be in establishing the structure of complexes when the magnetic properties known are aided with electronic spectral studies.

Molar Conductivity Measurements

Molar conductance gives information regarding the electrolytic property of a complex, whether it is an electrolyte or non-electrolyte. Standard values of molar conductance calculated in different solvents are available[53] for comparision with the experimental values. When the electrolytic nature of the complex is known it helps in distinguishing those groups that are involved in coordination to the central metal ion and groups outside the coordination sphere. When all the groups are involved in coordination the complex behaves as a non electrolyte. Thus molar conductivity measurement is an additional tool in determining the geometry of a complex.

In order to measure the molar conductivity ($-\Lambda-$ m) of a solution the conductivity of the solution has to be determined. For this the solution is placed in a cell, the cell constant of which has been determined by calibration with a solution of accurately known conductivity e.g. a standard potassium cholride solution. The resistance or conductance of a solution is measured with the help of a conductivity bridge from which the molar conductance is calculated by eqation 11

$$-\Lambda-m = 1000\ k/c \qquad \text{----------(11)}$$

where $-\Lambda-m$ is the molar conductivity in $ohm^{-1}\ cm^{2}\ mol^{-1}$, k is the specific conductance or conductivity in $ohm^{-1}\ cm^{-1}$ and c is the concentration in mol per litre.

EXPERI MENTAL

Reagents Used :-

The reagents used for the reactions described in this text were purified or dried wherever it was necessary.

Ethylenediamine [E.Merck], Formaldehyde [E.Merck], Benzidine [S D's Fine. Chem. PVT Ltd] were commercially pure samples and used as such. The metal salts $NiCl_2.6H_2O$ [E.Merck], $CoCl_2.6H_2O$ [S D's Fine. Chem. PVT Ltd], $CuCl_2.2H_2O$ [BDH] were practical grade which were recrystalysed before use. Solvents benzene, methanol, THF, DMF, MeCN, $CHCl_3$, DMSO and n-hexane were purified and dried by literature methods.

1. Template synthesis of dichloro [1,8- bis(biphenyl amino) [1,3,6,8,10,13] hexaaza cyclotetradecane] Metal(II) [ML_1Cl_2] [M=Co(II), Ni(II), Cu(II)]

Ethylenediamine [0.65 ml, 10 mmol] was injected to a solution of nickel chloride [1.185 gm, 10 mmol] dissolved in 30 ml methanol with continuous stirring at room temperature. The colour changes from light green to dark blue. Formaldehyde [2 ml, 20 mmol] was then added drop wise with continuous stirring. To the reaction mixture benzidine [1.84 gm, 10 mmol] dissolved in minimum quantity of methanol was added at room temperature which changed the solution to dark grey colour. The mother liquor was stirred overnight giving dark grey solid material which was filtered, washed with methanol, vaccum dried and kept in desiccator.

2. Synthesis of 1',8'-biphenyl bis(1,9-diamino[3,5,7] triaza nonane) [L_2]

30 ml of distilled methanol was taken in a round bottomed flask fitted with condenser. To a continously stirred solution of benzidine [0.9216 g, 5 mmol] in 30 ml methanol, ethylenediamine [1.32 ml, 20 mmol] was added drop wise. The reaction was exothermic and the

solution was stirred for a few minutes to bring it to room temperature. Now formaldehyde [2 ml, 20 mmol] was dropped in this reaction mixture which was refluxed for 24 hours. The reaction mixture was filtered to remove any suspension. Perchloric acid [2 ml, 20 mmol] dissolved in 10 ml methanol was added to the filtered mother liquor with vigourous stirring at room temperature. It was stirred for an additional 30 minutes and the brown precipitate formed was filtered, washed with methanol, vaccum dried and kept in desiccator.

3. tetra chloro/perchlorato [1',8'-biphenyl bis(1,9,diamino [3,5,7] triaza nonano)] dimetal(II). $[M_2L_2X_4]$ [M=Co(II), X=Cl; Ni(II), $X=ClO_4$; Cu(II), X=Cl]

Ethylenediamine [1.32 ml, 20 mmol] was injected to a solution of nickel chloride [2.37 gm, 10 mmol] dissolved in 30 ml methanol with continuous stirring at room temperature. The colour changes from light green to dark blue. Formaldehyde [2 ml, 20 mmol] was then added drop wise with continuous stirring. To the reaction mixture benzidine [0.9216 g, 5 mmol] dissolved in minimum quantity of methanol was added at room temperature. The reaction mixture was stirred for an

additional one hour. Sodium perchlorate [1.49 gm, 10 mmol] dissolved in minimum quantity of methanol was then added which changed the solution to dark grey colour. The mother liquor was stirred overnight giving dark grey solid material which was filtered, washed with methanol, vaccum dried and kept in desiccator.

4. Synthesis of dichloro [8'-amino 1'-(1,9 diamino [3,5,7] triaza nonano) biphenyl] Metal(II).[ML_3Cl_2] [M=Co(II), Ni(II), Cu(II)]

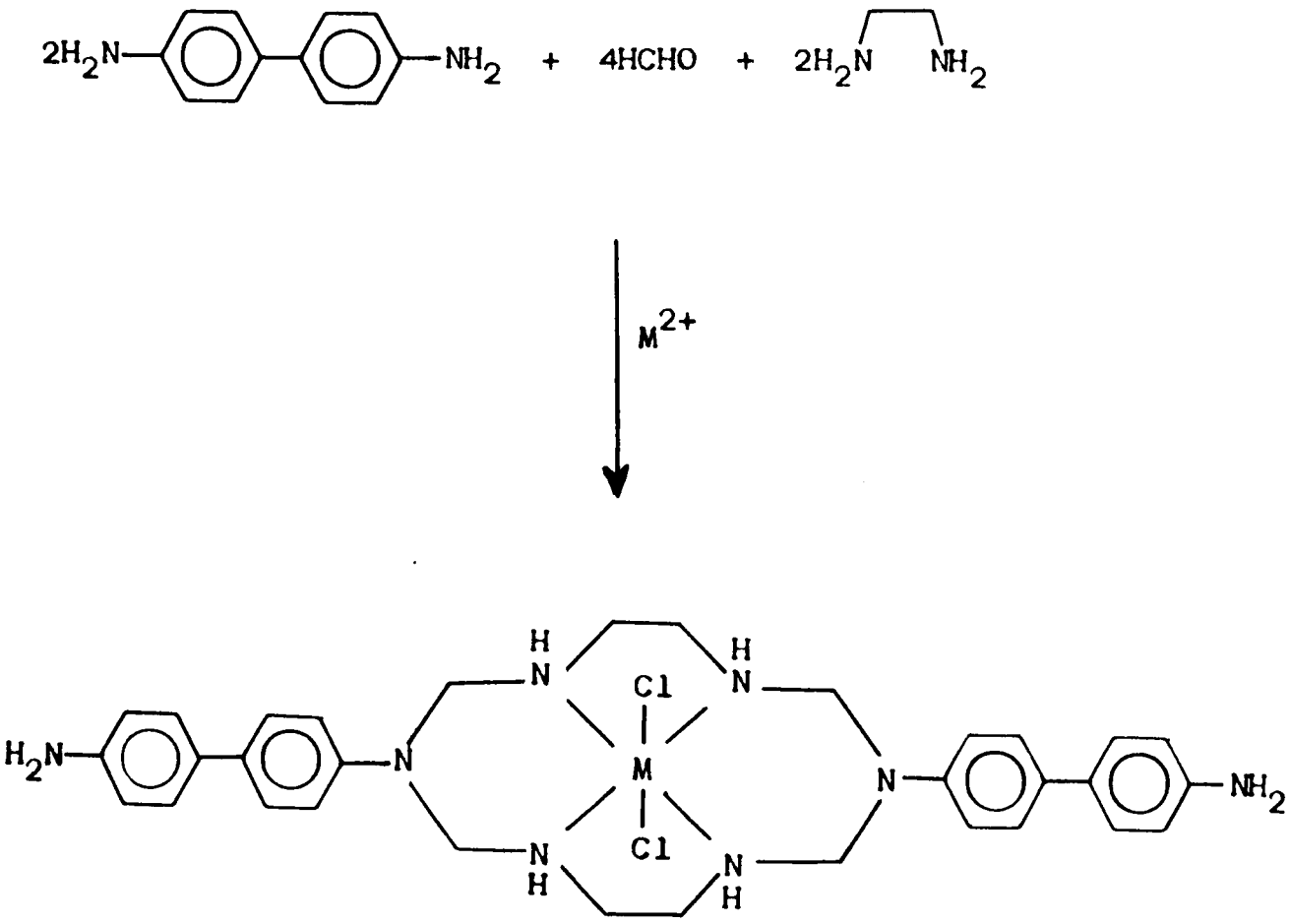
Ethylenediamine [1.32 ml, 20 mmol] was injected to a solution of nickel chloride [2.37 gm, 10 mmol] dissolved in 30 ml methanol with continuous stirring at room temperature. The colour changes from light green to dark blue. Formaldehyde [2 ml, 20 mmol] was then added drop wise with continuous stirring. To the reaction mixture benzidine [1.84 g, 10 mmol] dissolved in minimum quantity of methanol was added at room temperature which changed the solution to dark grey colour. The mother liquor was stirred overnight giving dark grey solid material which was filtered, washed with methanol, vaccum dried and kept in desiccator.

RESULT AND DISCUSSION

dichloro [1,8-bis(biphenyl amino)[1,3,6,8,10,13] hexaaza cyclotetradecanel Metal(II). $[ML_1Cl_2]$ [M = Co(II), Ni(II), Cu(II)]

The novel hexaaza macrocyclic complexes of the type $[ML_1Cl_2]$ [M = Co(II), Ni(II), Cu(II)] were obtained by employing the metal template condensation reaction of ethylenediamine, formaldehyde and benzidine with 1:2:1 molar ratio in methanol medium and there by signifying the important role of the metal ion in the cyclization process. However, an attempt to synthesize a 14-membered hexaaza macrocyclic ligand 1,8-bis (biphenyl amino)[1,3,6,8,10,13] hexaaza cyclo tetradecane, L_1 by the condensation reaction of ethylenediamine, formaldehyde and benzidine could not prove successful and the reaction did not produce the ligand L_1. The synthesized metal complexes have been characterized using physico-chemical methods as discussed below.

The result of elemental analyses and molecular weight determination (Table 1) suggest that the proposed macrocyclic complexes have 1:1 metal to ligand stoichiometry as shown in scheme 3. The compounds are slightly soluble in DMF and MeCN and freely soluble in



Scheme-3

DMSO. The molar conductance values of $[ML_1Cl_2]$ appeared in the region 19 to 30 ohm^{-1} cm^2 mol^{-1} which indicate that they are non-electrolytes[53] in DMSO (Table 1).

The preliminary identification of the macrocyclic complexes have been inferred from IR spectra. The main bands and their assignments are listed in table 2. The IR spectra of all the macrocyclic complexes do not show any peak corresponding to carbonyl group, instead a new single sharp medium intensity band in the region 3250-3210 cm^{-1} which can be attributed[44] to N-H stretching mode of the coordinated secondary amines. This strongly suggest that the proposed ligand framework is formed. However, the appearence of a doublet at 3380-3350 cm^{-1} in all the macrocyclic complexes may be due to the N-H stretching frequency of the primary amino groups of the benzidine moiety. The IR absorption bands in 2950-2900 cm^{-1} and 1450-1410 cm^{-1} region absorbed in all the complexes may reasonably be assigned to C-H stretching and C-H bending vibrational modes. The band corresponding to phenyl group vibration and N-H deformation appeared at their expected positions (Table 2). The presence of a sharp band at 420-380 cm^{-1} in all

the macrocyclic complexes is due to the M-N stretching vibration.[54] However a medium band in the frequency region 280-250 cm^{-1} has been assigned as M-Cl stretching vibration.

The mode of coordination of the ligand and the stereochemistry around the transition metal ion was further confirmed by magnetic moment measurements and ligand field spectroscopic studies as discussed below.

The observed values of magnetic moments for the macrocyclic cobalt(II) complexes appeared in the range expected for three unpaired electrons (Table 3). The electronic spectra (Table 3) of cobalt(II) complex gave two bands which lie at 22100 and 17200 cm^{-1} which may be ascribed to the $^4T_{1g}(F)$ ------> $^4T_{2g}(P)$ and $^4T_{1g}(F)$ ------> $^4A_{2g}(F)$ transition, respectively. This strongly suggests[51,54] the octahedral geometry around the cobalt(II) ion. The macrocyclic complex of nickel(II) shows magnetic moment of 3.12 B.M. which correspond to spin free complex. However, the electronic spectrum shows three distinct bands consistent with the spectral features of the octahedral nickel(II) complexes.[55,56]

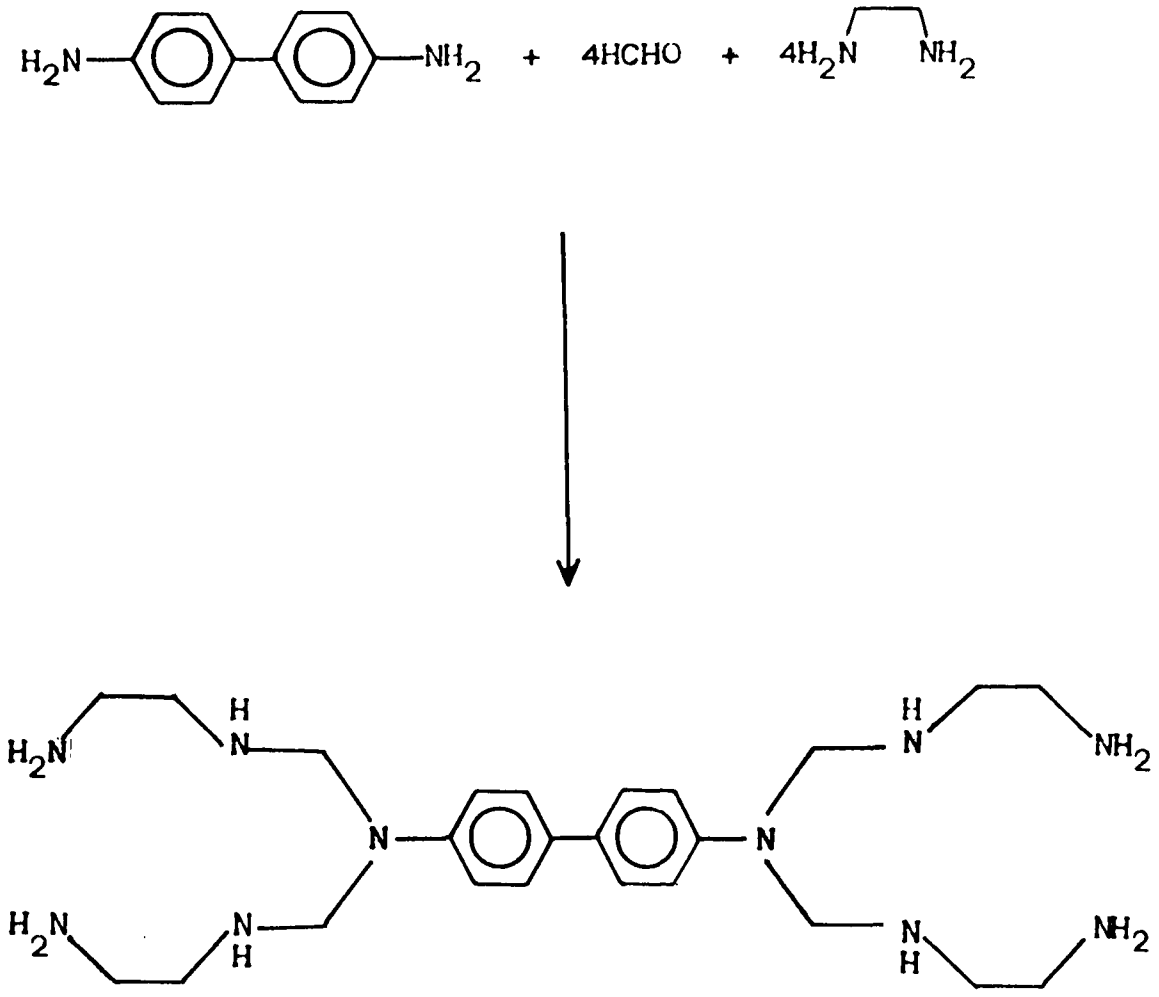
The broad band around 11000 cm^{-1} and two intense band around 20000 and 27500 cm^{-1} may reasonably be assigned to $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$ trasitions, respectively.

The electronic spectrum of macrocyclic copper(II) complex show a broad band maximum (Table 3) at 19400 cm^{-1} with a shoulder at 16300 cm^{-1} which may unambegiously be assigned to $^2B_{1g} \longrightarrow {}^2E_g$ and $^2B_{1g} \longrightarrow {}^2B_{2g}$ transitions, respectively corresponding to a distorted octahedral geometry around the copper(II) ion. The magnetic moment value further confirm the above proposed geometry. Strikingly all the macrocyclic complexes exhibit strong absorptions around 30000 cm^{-1} which may be due to a charge transfer band.

1',8'- biphenyl bis (1,9-diamino[3,5,7] triaza nonane)

The condensation reaction of ethylenediamine and formaldehyde with benzidine in methanol as solvent gives the title compound L_2 as shown in scheme 4.

The results of elemental analyses and molecular weight data confirm the proposed stoichiometry of the

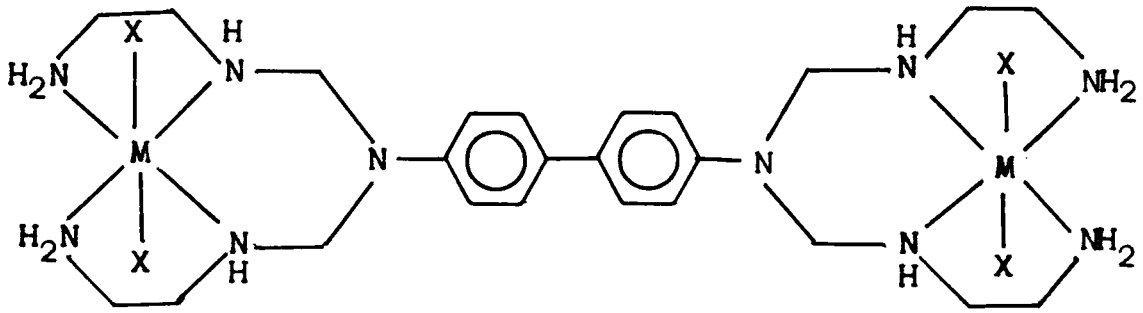


Scheme-4

ligand L_2.The ligand has been characterized by IR spectrscopic studies. The important frequencies observed in the IR spectrum (Table 2) are a doublet at 3400 cm^{-1} and a sharp single band at 3250 cm^{-1} which may reasonably be assigned to N-H stretching frequencies of primary and secondary amino groups, respectively. A medium band which appeared at 1625 cm^{-1} may be assigned to the N-H bending vibration of the amino groups. The band corresponding to ν(C-H) and ν(C-N) vibration were observed at their expected[57] position (Table 2). The phenyl ring vibrations of the ligand showed[58] three bands at 1420,1080 and 730 cm^{-1}.

tetra chloro/perchlorato [1',8'-biphenyl bis(1,9,diamino [3,5,7] triaza nonano)] dimetal(II). $[M_2L_2X_4]$ [M=Co(II), X=Cl; Ni(II), X=ClO_4; Cu(II), X=Cl]

The overall geometry and mode of bonding of these metal complexes have been characterized by elemental analyses, IR and electronic spectral studies as well as magnetic moment and molar conductance measurements. The elemental analysis and molecular weight data supports the proposed structure as shown in fig 15.



M = Co(II), X = Cl

M = Ni(II), X = ClO_4

M = Cu(II), X = Cl

Fig. - 15

All these complexes are insoluble in water and organic solvents except DMSO. The molar conductance values observed (Table 1) for all the complexes suggest their non-electrolytic nature.

The major change noticed in the IR spectra (Table 2) of these metal complexes is the negative shift in ν(N-H) by 50-30 cm^{-1} in comparison to the metal free ligand. This strongly suggests the involvement of all the nitrogens in coordination to the metal ion. This has been further confirmed by the appearance of a new medium intensity band in the region 380-350 cm^{-1} for all the metal complexes which can be assigned to M-N stretching vibration.[59] However,a medium intensity band at 300-280 cm^{-1} may, unambegiously, be assigned[60] to M-Cl stretching mode. All other bands in this complexes do not show any appreciable change when compared to their free ligand.

The IR spectra of the complex $[Ni_2L_2(ClO_4)_4]$ shows two bands at 1040 and 980 cm^{-1} which are consistent with the perchlorate group vibration corresponding[61] to ν_3 and ν_4. The magnetic susceptibility (Table 3)

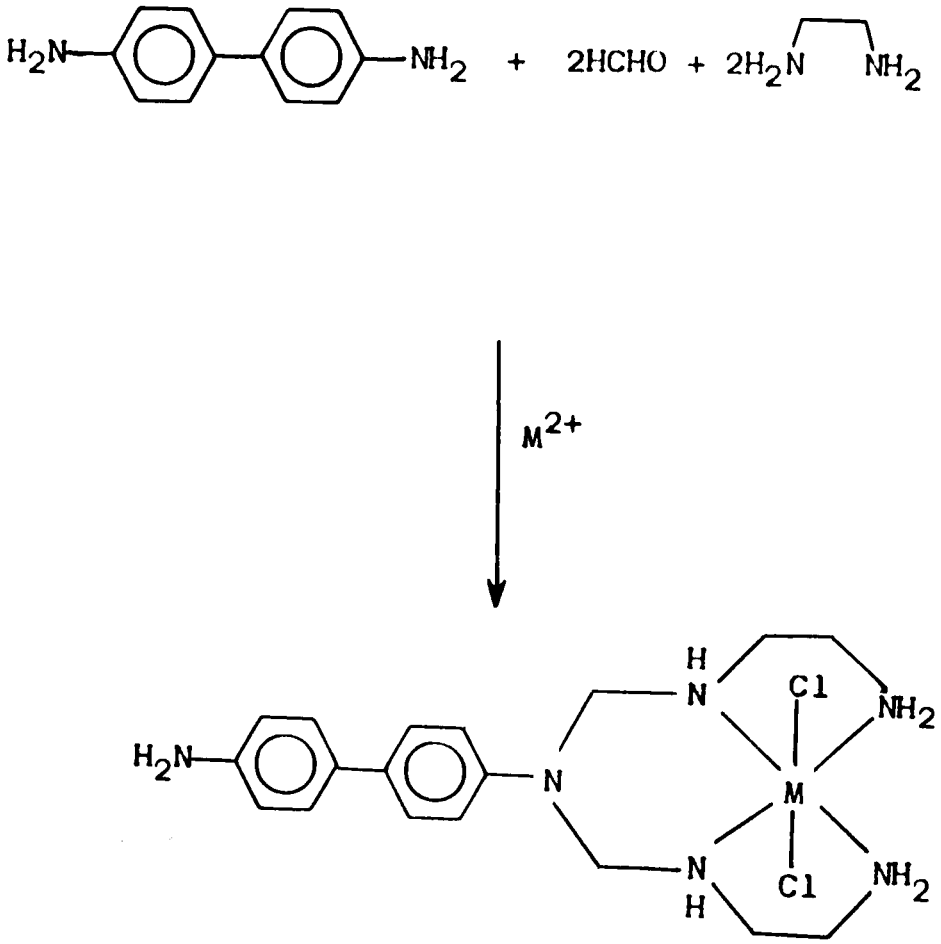
measurement for all these bimetallic complexes are found to be normal which suggest the absence of any strong interaction between the electrons of the two metal centres.

The electronic spectrum of the dicobalt(II) complex gave two ligand field bands at 22100 and 13150 cm^{-1} which may be assigned to $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$ transitions, respectively consistent with an octahedral geometry around the cobalt(II) ion. The band expected at 8000 cm^{-1}could not be recorded as it occurs beyond the range of the instrument used. The magnetic moment data confirm the above proposed geometry. The dinickel(II) complex is of spin free type and shows magnetic moment of 3.05 B.M. The electronic spectrum of this complex shows two distinct bands and clearly approach[56,62] the spectral features of octahedral Ni(II) complex. A broad band appeared around 11500 cm^{-1} and an intense band at 27750 cm^{-1} which may be assigned to $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$ transitions, respectively.

The observed magnetic moment for dicopper(II) complex corresponds to distorted octahedral d^9 system. The electronic spectrum exhibits a broad band maximum at 19400 cm^{-1} and a shoulder at 16300 cm^{-1} which may reasonably be assigned to $^2B_{1g}$ ------> ^2E_g and $^2B_{1g}$ -----> $^2B_{2g}$ transitions, respectively further substantiates the distorted octahedral geometry around a metal ion.[56] The large intensity band observed for all the complexes show their considerable charge transfer character.

dichloro [8'-amino 1'-(1,9 diamino[3,5,7] triaza nonano) biphenyl] Metal(II) $[ML_3Cl_2]$ [M=Co(II), Ni(II),Cu(II)]

Molecular formulae of the complexes $[ML_3Cl_2]$ [M=Co(II), Ni(II), Cu(II)] have been assigned on the basis of the results of their elemental analysis and the molecular weight data (Table 1) which suggest 1:1 metal to ligand stoichiometry as shown in the scheme 5. All the complexes are insoluble in common organic solvents but moderatly soluble in MeCN, DMF, $CHCl_3$ and freely soluble in DMSO. The molar conductance measurements in DMSO are low (Table 1) suggesting that the complexes are non-electrolytes.[53]



Scheme-5

The major IR spectral features of the metal complexes are listed in Table 2. A new single sharp band for all the complexes appeared in the region 3230-3180 cm^{-1} when compared with the reactants used and can be assigned[44] to coordinated N-H stretching frequency of secondary amines. The appearance of two doublet in the region 3340-3310 cm^{-1} and 3400-3370 cm^{-1} may be assigned to the coordinated primary amines and the free primary amines of the benzidine moiety. The IR spectra of all the complexes exhibit band in the region 1640-1610 cm^{-1} which is assignable to N-H deformation mode. This information along with the appearance of a medium intensity band in the region 390-360 cm^{-1} may be attributed to the νM-N vibration which strongly ascertain the involvemenmt of the nitrogen in coordination to the metal centres. The presence of bands in the region 300-270 cm^{-1} in all the complexes originate[63] from νM-Cl vibration.

The overall geometry of these complexes have been deduced on the basis of the observed values of the magnetic moments and the band positions in the electronic spectra.

The magnetic moment values correspond to high spin d^7, d^8 and d^9 system consistent with the octahedral environment around cobalt(II), nickel(II) and copper(II). The electronic spectrum of cobalt(II) complex exhibit two bands at 22200 and 17000 cm^{-1} which may reasonably be assigned to $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$, transitions respectively. However the electronic spectrum of the nickel(II) complex shows ligand field bands in 27700, 20000 and 11900 cm^{-1} which may be attributed to $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ transitions, respectively. The electronic spectrum of copper(II) complex exhibits a broad band maxima at 19600 cm^{-1} and a shoulder at 15600 cm^{-1} may unambegiously be assigned to $^2B_{1g} \longrightarrow {}^2E_g$ and $^2B_{1g} \longrightarrow {}^2B_{2g}$ transitions, respectively which suggest a distorted octahedral geometry around the metal ion. All the complexes show a large intensity band around 32000 cm^{-1} which may be due to the charge transfer transition.

Table- 1

Analytical data of L_2, ML_1Cl_2, $M_2L_2Cl_4$, $M_2L_2(ClO_4)_4$, ML_3Cl_2.

Ligand/Complexes	Colour	M.Pt °C	Λ_m $\Omega^{-1}Cm^2\ Mol^{-1}$	Found (Calcd) %					Mol. Wt.
				H	N	M	Cl		
L_2	Orange	124	-	60.95 (61.01)	9.25 (9.32)	29.59 (29.66)	-	-	471 (472)
$[Co\ L_1\ Cl_2]$	Brown	238	30	57.60 (57.65)	5.85 (6.00)	16.32 (16.81)	8.55 (8.85)	10.60 (10.66)	663 (666)
$[Ni\ L_1\ Cl_2]$	Brown	216	19	57.65 (57.70)	5.89 (6.01)	16.70 (16.82)	8.69 (8.79)	10.50 (10.66)	664 (665.5)
$[Cu\ L_1\ Cl_2]$	Black	>350	25	57.22 (57.27)	5.90 (5.96)	16.61 (16.70)	9.45 (9.47)	10.49 (10.59)	669 (670.5)
$[Co_2\ L_2\ Cl_4]$	Brown	240	35	39.14 (39.34)	5.06 (6.01)	19.01 (19.13)	15.99 (16.12)	19.31 (19.40)	730 (732)
$[Ni_2\ L_2(ClO_4)_4]$	Grey	250	30	28.95 (29.17)	4.05 (4.45)	14.11 (14.18)	11.65 (11.85)	14.30 (14.38)	985.5 (987)
$[Cu_2\ L_2\ Cl_4]$	Black	290	32	38.70 (38.86)	5.82 (5.93)	18.80 (18.89)	17.01 (17.13)	19.05 (19.16)	739.5 (741)
$[Co\ L_3\ Cl_2]$	Brown	220	34	47.02 (47.16)	6.10 (6.11)	18.30 (18.34)	12.60 (12.88)	15.45 (15.50)	457 (459)
$[Ni\ L_3\ Cl_2]$	Brownish Cream	235	12	46.95 (47.21)	6.02 (6.12)	18.26 (18.36)	13.62 (12.79)	15.32 (15.52)	456 (457.5)
$[Cu\ L_3\ Cl_2]$	Black	170	25	46.52 (46.70)	5.89 (6.05)	17.96 (18.16)	13.59 (13.72)	15.29 (15.35)	460 (462.5)

Table -2

IR Spectral data of L_2, ML_1Cl_2, $M_2L_2Cl_4$, $M_2L_2(ClO_4)_4$, ML_3Cl_2

Ligand/Complexes	C-H	NH/NH_2	C-N	δN-H	M-N	M-Cl	Ring Vibrations
L_2	2910	3250 3400	1170	1625	-	-	1420 1090 730
[Co L_1 Cl_2]	2920	3230 3380	1180	1650	420	260	1430 1050 760
[Ni L_1 Cl_2]	2900	3210 3370	1200	1650	390	280	1410 1060 740
[Cu L_1 Cl_2]	2950	3250 3350	1210	1610	380	250	1420 1080 780
[Co_2 L_2 Cl_4]	2930	3200 3350	1190	1640	390	290	1440 1030 750
[Ni_2 $L_2(ClO_4)_4$]	2910	3200 3350	1200	1630	350	300	1420 1040 770
[Cu_2 L_2 Cl_4]	2920	3210 3370	1200	1630	360	280	1440 1050 730
[Co L_3 Cl_2]	2920	3230 3340 3400	1180	1610	370	300	1410 1030 750
[Ni L_3 Cl_2]	2940	3190 3310 3370	1190	1630	360	290	1490 1080 730
[Cu L_3 Cl_2]	2910	3180 3300 3390	1220	1640	390	270	1410 1070 700

Table- 3

Magnetic moment values, electonic spectral (cm^{-1}) data and their assignments.

Complexes	μeff.	Band Position (Cm^{-1})	Assignments
[Co L_1 Cl_2]	4.05	22100 17200	$^4T_{1g}(F)$ ------> $^4T_{1g}(P)$ $^4T_{1g}(F)$ ------> $^4A_{2g}(F)$
[Ni L_1 Cl_2]	3.12	27500 20000 11000	$^3A_{2g}(F)$ ------> $^3T_{1g}(P)$ $^3A_{2g}(F)$ ------> $^3T_{1g}(F)$ $^3A_{2g}(F)$ ------> $^3T_{2g}(F)$
[Cu L_1 Cl_2]	1.70	18600 16300	^2B1g ------> ^2E_g $^2B_{1g}$ ------> $^2B_{2g}$
[Co_2 L_2 Cl_4]	4.41	22100 13150	$^4T_{1g}(F)$ ------> $^4T_{1g}(P)$ $^4T_{1g}(F)$ ------> $^4A_{2g}(F)$
[Ni_2 L_2 $(ClO_4)_4$]	3.05	27750 11500	$^3A_{2g}(F)$ ------> $^3T_{1g}(P)$ $^3A_{2g}(F)$ ------> $^3T_{2g}(F)$
[Cu_2 L_2 Cl_4]	1.82	19400 16300	$^2B_{1g}$ ------> ^2E_g $^2B_{1g}$ ------> $^2B_{2g}$
[Co L_3 Cl_2]	4.82	22000 17000	$^4T_{1g}(F)$ ------> $^4T_{1g}(P)$ $^4T_{1g}(F)$ ------> $^4A_{2g}(F)$
[Ni L_3 Cl_2]	3.25	27700 20000 11900	$^3A_{2g}(F)$ ------> $^3T_{1g}(P)$ $^3A_{2g}(F)$ ------> $^3T_{1g}(F)$ $^3A_{2g}(F)$ ------> $^3T_{2g}(F)$
[Cu L_3 Cl_2]	1.79	19600 15600	$^2B_{1g}$ ------> ^2E_g $^2B_{1g}$ ------> $^2B_{2g}$

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